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(NEW WORLD VISTAS) Theory of Anion-Substituted Nitrogen Bearing III-V Alloys

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Bandstructure calculations of dilute alloys of nitrogen-rich GaNP and GaNAs were performed. Because of the large bond-length mismatch between nitrogen (N) and phosphorous (P) or arsenic (As), enormous internal strains strongly inhibit the miscibility of the latter into the anion lattice. This report discusses the thermodynamic behavior of incorporation of P or As into the III-N lattice by calculating the miscibility gaps in the regular solution model. The band states show some remarkable behavior when small amounts of P or As are substituted for N; resonances at the valence band edge exhibit characteristics which are somewhere between that of a hydrogenic defect and a propagating state one usually finds at the band edge of an alloy.

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19 January 1998

Mr. Mike Prairie
AFOSR
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Dear Mike,

I am enclosing two documents. A copy of our final report on the anion substituted alloys, and a copy of a set of calculations done by An-Ban Chen. There is still a bit of work to do to firm up conclusions from the two different approaches, but here is a preliminary try. I do not expect that these conclusions will change much as we refine the supporting results. To keep this discussion to a finite length I will only talk about the GaNAs alloy.

1. When 1% As is substituted into GaN in a regular array there is a state introduced into the gap 0.2 eV above the valence band edge. (Zunger claims this state is 0.8 eV above the valence band edge.). This could have useful applications in Lasers by increasing the density of final states and possibly the transition matrix elements thereby increasing the gain. It will also localize exciton states, which again will benefit laser gains.
2. When the As concentration is raised to about 4%, again in a regular array, the gap closes.
3. However, even though the alloy scattering strength An-Ban used in his calculations corresponds to the situation with only near neighbor relaxation, so it is likely to be overestimated, the full CPA calculation still does not predict that the band gap goes to zero. An-Ban's result agrees with Mark's in the low concentration (1%) limit, and disagrees with the Zunger group's result. The bottom line is that for a random alloy the gap does not close, but for an ordered array it does. Since at low concentrations the correlation should be small, the random result is likely to be the more realistic one. Should that prove out when we finish the refinements, it means that the gap never goes lower than 0.8 eV even if a concentrated alloy can be made.
4. An-Ban also calculates the alloy scattering rate, and for 10% As in GaN concludes that for holes it is 10^{-14} sec. With that scattering rate the hole mobility will be miserable.

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5. Thinking about how to realize the goal of closing the gap, it seems probable from the theoretical results that the simple ternary $\text{GaN}_{1-x}\text{As}_x$ cannot accomplish this, even if it could be grown with x close to 0.5 (which is in itself unlikely).
6. However, let us consider the following:
 - 6.1 the energetics governing the alloy formation stem from strain, and are largely short-ranged
 - 6.2 the gap bowing stems mostly from the large difference in on-site Hamiltonian, i.e. these alloys fall in to the category of the "strong scattering" limit. Strain modifies things, but is a second-order effect. We can exploit the fact that the mechanisms governing these two properties are distinct. We suggest the following:
 - (a) Start from InN (gap is $\sim 2\text{eV}$), instead of GaN
 - (b) Incorporate about 10% As into InN, and at the same time add about 10% Ga. The Ga will act to relieve the strain, making the As easier to incorporate, but will not increase the fundamental InN gap much. The addition of As will produce the same strong bowing as in GaN, and since the starting gap is less (2 eV vs 3.5eV), it should be possible to bow the gap approximately to zero with 10% As.

While we still have a little work to firm all this up, I think once this is done we will have answered the questions you originally posed to us, plus a few we did not anticipate.

I would be happy to answer any questions you have. Needless to say we are interested in any further support you can give us in related areas. I think there may be some real benefits to GaN laser gains from the additions of small amounts of As or P.

It may also be possible to reach your IR material goals by adding N to GaInAs alloys.

Regards,


Arden Sher
Associate Director
Applied Physical Sciences Laboratory

AS/ns

Enclosures

Anion Substituted III-V Nitride Alloys

Recently Bellaiche, Wei and Zunger (BWZ) [1] have studied the band gap states of $\text{GaAs}_{1-x}\text{N}_x$ and $\text{GaAs}_{1-x}\text{N}_x$. In their work, fitted pseudopotentials and a constrained plane-wave set were employed in large supercell calculations to obtain the highest valence band and lowest conduction band energies (at $\mathbf{k}=0$) in several random configurations for a given alloy concentration. They have found several interesting results: large bowing parameters, strong variation of bowing parameters with concentration, and localization of valence-top states in the dilute As or P cases. They have also shown that, when the alloys structures are conformed to the substrates, the calculated gaps agreed reasonably with the measured gaps for several alloys with low N concentrations. It is thus interesting to see if the same qualitative physics can be obtained from a completely different approach that we have been using - the average Green function approach based on the molecular coherent potential approximation (MCPA) and a hybrid pseudo-potential tight binding band scheme (HPTB). We note that the average Green function can yield the whole alloy energy spectra, not just the band edges. It also provides the important information about the life time of Bloch states due to alloy disorder.

The band structures based on HPTB are obtained in a similar manner as that described in our book [2], with the input band structures deduced from a combination of the available theoretical and experimental (very little) results [3]. Figures 1 through 3 show the band structure constructed for AlN, GaN, and InN respectively.

The band structure parameters for the nitride compounds are then used along with those of the other III-V compounds obtained in [2] in the MCPA calculation. In this approach, a molecular unit consists of eight hybrid orbitals along the four tetrahedral bonds surrounding each alloying atom (the anions in the present case). The differences in the intra-molecular TB matrix elements between the two different molecular units are the alloy scattering potentials. The fluctuations in these matrix elements arise from two origins: the difference in the atomic term values and the first-neighbor interactions which depend on the pairs of atoms considered and the bond lengths governed by a bimodal bond-length distribution in the alloy. Here we focus on GaAsN alloys, for which the scattering parameters are given in Table 1. Similar results for other anion-substituted nitride alloys can also be generated if needed.

*Table 1. Alloy disordered parameters as defined in Eq.(5.11.2)
in Ref [2] for $\text{GaAs}_{1-x}\text{N}_x$ at $x=0.5$*

representation	δ (eV)	Δ (eV)
Γ_6	-5.593	0.257
Γ_7	-2.856	-0.153
Γ_8	-3.212	-0.2153

The scattering parameters shown in Table 1 indicate that these alloys are strong-scattering alloys as compared to all the cases studied in [2]. While the atomic t-matrix approximation (ATA) and CPA gave virtually the same results for all the III-V alloys studied in [2] (because alloy scattering is weak), ATA is not adequate for the present study. Therefore, a complete MCPA calculation, which is computationally much more expensive than ATA, has to be carried out.

Figure 4 shows the plots of spectral density of states (DOS) in the energy range around the band gap for $\text{GaAs}_{1-x}\text{N}_x$ at $\mathbf{k}=(0,0,0)$ for $x=0.1, 0.5$ and 0.9 . The arrows indicate the delta-functions corresponding to the band structures in the virtual crystal approximation (VCA). Since the spin-orbital coupling is included, the three VCA energies from lower to higher energies correspond to Γ_7 (2-fold), Γ_8 (4-fold), and Γ_6 (2-fold) states respectively. While the Γ_6 spectral DOS remains reasonable sharp, the Γ_7 and Γ_8 spectral DOS are broadened substantially. We note that at the bottom panel the spin-orbit splitting is very small, the two peaks are not the Γ_7 and Γ_8 respectively; they represent the split-band caused by the strong alloy scattering. This split-band limit is also evident from the bottom panel in Figure 5 where total density of states is plotted.

Given the broadened spectral DOS, it is not unambiguous to define the band gap. Within the present frame work, there are two possible choices: the energy separation between the peaks or that between the two edges of the Γ_6 and Γ_8 spectral DOS. Neither choice is unique and also there is no unique way to define the edges. The bottom line marked by 'edge' in Figure 6 is the separation between the edges chosen at the energies where the spectral DOS has a value of 0.5 of scale used in Figure 5. This is about the uncertainty in the magnitude of the calculated spectral DOS. Also plotted in Figure 6 are the energy separation between the two peaks (the curve marked by 'peak') and the band gap in VCA. The several experimental gaps available all lie between the two lower curves but closer to the bottom one.

From the physics point of view, this is an interesting case because it is the first pseudo-binary semiconductor alloy that has an alloy scattering potential strongly influencing the band-edge states, particularly the valence band top. These broadening in the spectral DOS implies that hole mobility is severely limited. Even though the broadening (≈ 0.1 eV, corresponding to 10^{-14} s in life time) in the spectral DOS for the conduction band edge is not as great as seen from Figure 4, it is significantly larger than other III-V alloys. Thus in terms of normal semiconductor application, this alloy is a poor one, not only with a limited mobility but also with a great difficulty of mixing (due to large lattice mismatch). However, there may be new application associated with the new features in the electronic structures such as band tails and large variation of band gap and mobility with concentration and temperature.

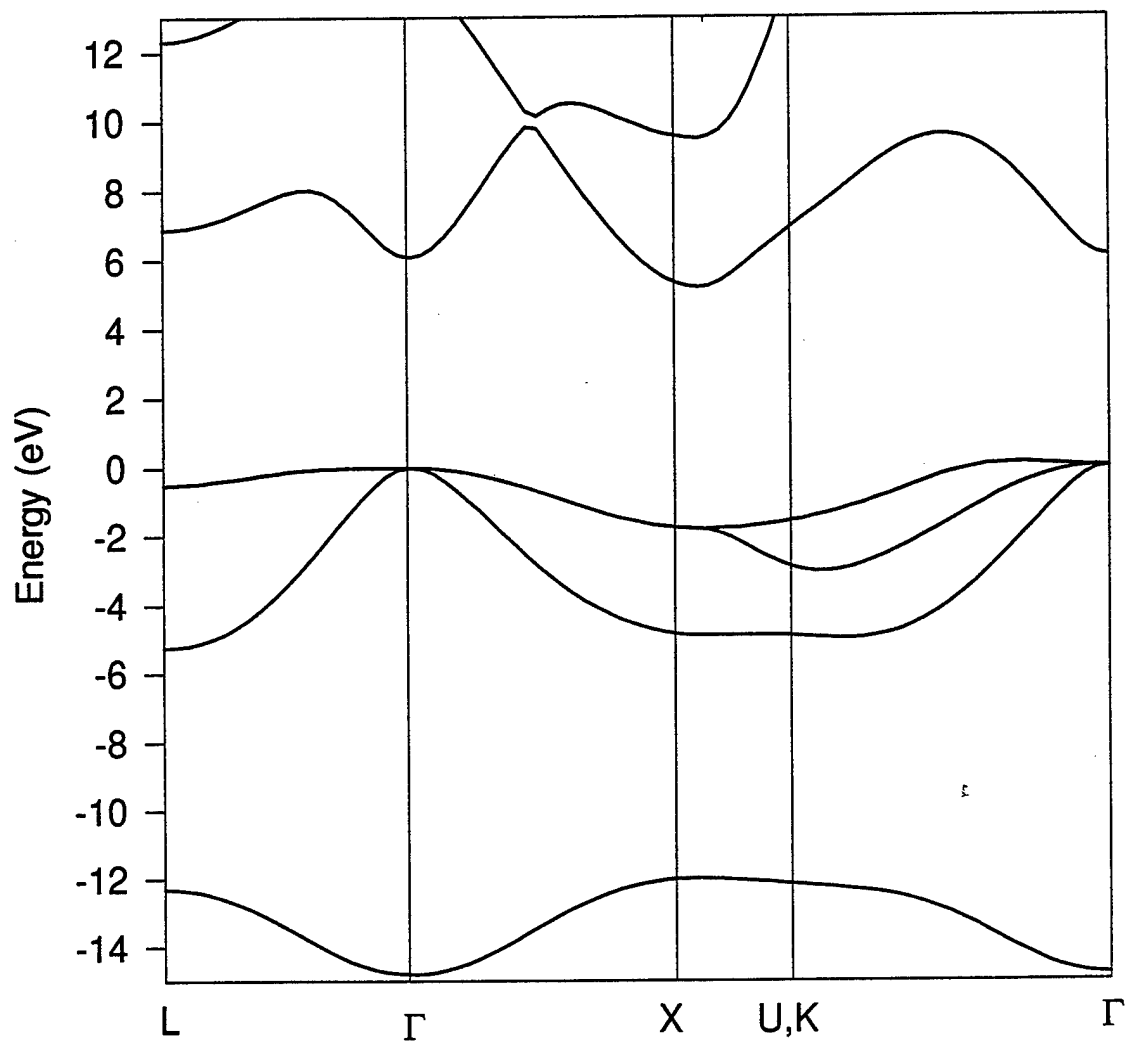
We note that the present MCPA study and BWZ's work are not adequate for the study of the band tail and the mobility edge. The CPA only effectively treats the extended states while BWZ only probes one or two states and is difficult to exhaust enough

configurations to be statistically significant. Both studies also have not explicitly included the d-states in the calculation, which may alter some of the above results.

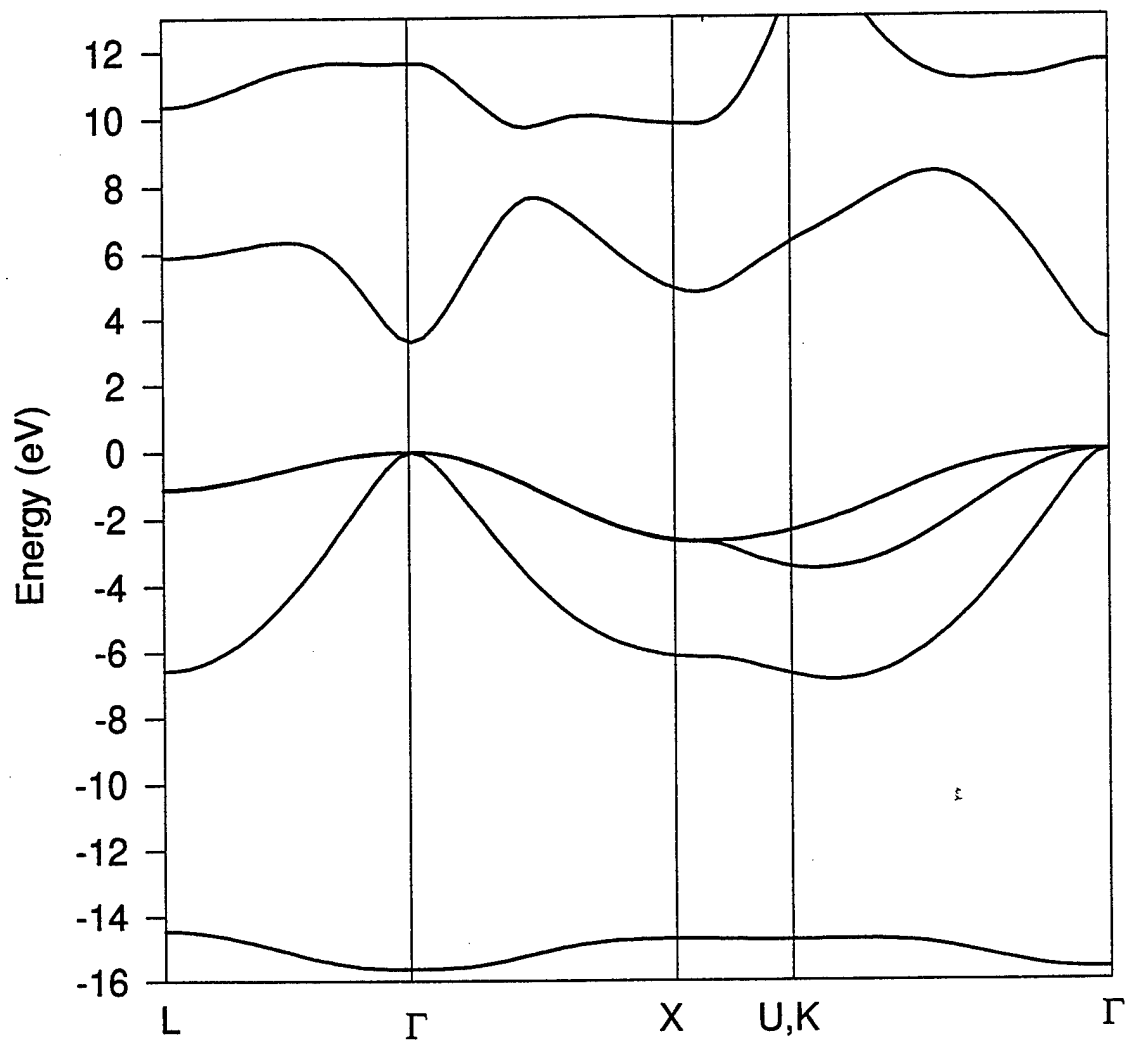
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- [2] A.-B. Chen and A. Sher, **Semiconductor Alloy** (Plenum Publ. Co., 1995).
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AlN



GaN



InN

